

## Appendix B

### PROPERTY MODELS

#### B.1 Thermodynamic Models

REFPROP calculates the thermodynamic properties using comprehensive equations of state. This approach ensures thermodynamic consistency and allows calculations at all conditions. Other approaches, such as the combination of a vapor-phase model with vapor pressure and liquid density equations may not be applicable in the compressed liquid and supercritical regions and do not always give reliable results for derived properties such as heat capacity and speed of sound.

##### B.1.1 Pure fluid equations of state

Three models are used for the thermodynamic properties of pure components, depending on the availability of data. The first is the modified Benedict-Webb-Rubin (MBWR) equation of state. This model was first proposed by Jacobsen and Stewart (1973) and has been applied to a wide variety of fluids, including hydrocarbons, cryogenic fluids, and refrigerants. It is capable of accurately representing the properties of a fluid over wide ranges of temperature, pressure, and density. The MBWR equation is the basis for the current international standard for the properties of R123 (Younglove and McLinden, 1994).

The MBWR equation expresses pressure as an explicit function of temperature and molar density and is of the form,

$$P = \sum_{n=1}^9 \alpha_n \rho^n + \exp\left[\left(\rho / \rho^{crit}\right)^2\right] \sum_{n=10}^{15} \alpha_n \rho^{2n-17}, \quad (1)$$

where the  $a_i$  are simple functions of temperature resulting in a total of 32 adjustable parameters. For a complete description of the energy quantities (enthalpy, entropy, etc.), the MBWR equation is combined with an expression for the molar heat capacity of the ideal-gas state, that is, vapor in the limit of zero pressure. A form combining polynomial and theoretical terms is used:

$$C_p^{id} = \sum_i c_i T^{t_i} + \sum_k \frac{u_k^2 \exp(u_k)}{[\exp(u_k) - 1]^2}, \quad (2)$$

with

$$u_k = \frac{c_k}{T}. \quad (3)$$

All of the thermodynamic properties can be computed from Eqs. (1–3), as detailed by Younglove and McLinden (1994).

The second high-accuracy pure-fluid equation of state is expressed in terms of reduced molar Helmholtz free energy:

$$a = \frac{A}{RT} = a^{id} + a^r = \ln \delta + \sum_i \alpha_i \tau^{t_i} + \sum_k \alpha_k \tau^{t_k} \delta^{d_k} \exp(-\gamma \delta^{l_k}), \quad (4)$$

where the first two terms on the right side of Eq. (4) constitute the ideal-gas contribution  $a^{id}$ . They are analogous to the combination of the  $a_1$  term in the MBWR equation of state ( $a_1 = RT$ ) and the ideal-gas heat capacity (Eqs. 2 and 3). The second summation is the residual, or real-fluid, contribution  $a^r$ . The temperature and density are expressed in the dimensionless variables  $\tau = T^*/T$  and  $\delta = \rho/\rho^*$ , where  $T^*$  and  $\rho^*$  are reducing parameters which are often, but not always, equal to the critical parameters. The  $\alpha_i$  and  $\alpha_k$  are numerical coefficients fitted to experimental data, and the exponents  $t_i$ ,  $t_k$ , and  $d_k$  are typically determined by a selection algorithm starting with a large bank of terms. The parameter  $\gamma$  is equal to

0 for terms with  $I_k = 0$ ; it is equal to 1 for terms with  $I_k \neq 0$ . This “Helmholtz-energy model” is the basis for the international standard formulation for R134a (Tillner-Roth and Baehr, 1994).

This model is sometimes termed the “fundamental equation” because it gives a complete description of the thermodynamic properties, as discussed by Tillner-Roth and Baehr (1994), but the MBWR equation of state combined with a  $C_p^{id}$  equation is entirely equivalent. The accuracies of these formulations vary, but those for R123 are typical: experimental data are reproduced with average absolute deviations of 0.04% for densities, 0.05% for vapor pressures, and 0.75% for heat capacities.

The third pure-fluid model is the extended corresponding states (ECS) model of Huber and Ely (1994). It is used for fluids with limited experimental data. Simple corresponding states is based on the assumption that different fluids obey, in reduced coordinates, the same intermolecular force law. This assumption leads to the conclusion that, with the appropriate scaling of temperature and density, the reduced residual Helmholtz energies and compressibilities ( $Z=p/RT\rho$ ) of the unknown fluid “ $j$ ” and a reference fluid “0” (for which an accurate, wide-ranging equation of state is available) are equal:

$$a_j^r(T_j, \rho_j) = a_0^r(T_0, \rho_0), \quad (5)$$

and

$$Z_j(T_j, \rho_j) = Z_0(T_0, \rho_0). \quad (6)$$

When combined with an expression for the ideal gas heat capacity (such as Eqs. 2 and 3), all other thermodynamic properties can be calculated. The reference fluid is evaluated at a “conformal” temperature and density:

$$T_0 = \frac{T_j}{f_j} = T_j \frac{T_0^{crit}}{T_j^{crit} \theta(T)}, \quad (7)$$

and

$$\rho_0 = \rho_j h_j = \rho_j \frac{\rho_0^{crit}}{\rho_j^{crit}} \phi(T). \quad (8)$$

where the multipliers  $1/f_j$  and  $h_j$  are termed reducing ratios. Simple corresponding states was developed for spherically symmetric molecules, for which the reducing ratios are simple ratios of the critical parameters. The ECS model extends the method to other types of molecules by the introduction of the “shape factors”  $\theta$  and  $\phi$ . These shape factors are taken here to be functions of temperature and density. The shape factors are fitted to experimental data, typically vapor pressures and saturated liquid densities. The reference fluid is chosen to provide the best fit of the data and is usually chemically similar to the fluid of interest.

### B.1.2 Mixture model

The thermodynamic properties of mixtures are calculated with a new model which was developed, in slightly different forms, independently by Tillner-Roth (1993) and Lemmon (1996, 1999). It applies mixing rules to the Helmholtz energy of the mixture components:

$$a_{mix} = \sum_{j=1}^n \left[ x_j (a_j^{id} + a_j^r) + x_j \ln x_j \right] + \sum_{p=1}^{n-1} \sum_{q=p+1}^n x_p x_q F_{pq} a_{pq}^{excess} \quad (9)$$

This mixing formula may be applied directly to the Helmholtz equation of state. Application to the MBWR equation of state and the ideal gas heat capacity expression used with the MBWR and ECS models requires transformations:

$$a^r = \frac{1}{RT} \int_V^\infty (P - RT\rho) dV, \quad (10)$$

$$a^{id} = \frac{h_{ref}}{RT} - \frac{S_{ref}}{R} - 1 + \ln \left( \frac{T\rho}{T_{ref}\rho_{ref}} \right) + \frac{1}{RT} \int_{T_{ref}}^T C_p^{id} dT - \frac{1}{R} \int_{T_{ref}}^T \frac{C_p^{id}}{T} dT \quad (11)$$

where  $h_{ref}$  and  $S_{ref}$  are an arbitrary reference enthalpy and entropy at the reference state specified by  $T_{ref}$  and  $\rho_{ref}$ .

The first summation in Eq. (9) represents the ideal solution; it consists of ideal gas (superscript  $id$ ) and residual or real fluid (superscript  $r$ ) terms for each of the pure fluids in the  $n$  component mixture. The  $x_j \ln x_j$  terms arise from the entropy of mixing of ideal gases where  $x_j$  is the mole fraction of component  $j$ . The double summation accounts for the “excess” free energy or “departure” from ideal solution. The  $F_{pq}$  are generalizing parameters which relate the behavior of one binary pair with another;  $F_{pq}$  multiplies the  $a_{pq}^{excess}$  term(s), which are empirical functions fitted to experimental binary mixture data. The  $a^r$  and  $a_{pq}^{excess}$  functions in Eqs. (9 and 10) are not evaluated at the temperature and density of the mixture  $T_{mix}$  and  $\rho_{mix}$  but, rather, at a reduced temperature and density  $\tau$  and  $\delta$ . These  $\tau$  and  $\delta$  are very much in the spirit of the conformal temperature and density of the ECS method and are a key innovation in this model. The mixing rules for the reducing parameters used in REFPROP are:

$$\tau = \frac{T^*}{T_{mix}}, \text{ with } T^* = \sum_{p=1}^n \sum_{q=1}^n k_{T,pq} x_p x_q \frac{1}{2} (T_p^{crit} + T_q^{crit}), \quad (12)$$

and

$$\delta = \frac{\rho_{mix}}{\rho^*}, \text{ with } \frac{1}{\rho^*} = \sum_{p=1}^n \sum_{q=1}^n k_{V,pq} x_p x_q \frac{1}{2} \left( \frac{1}{\rho_p^{crit}} + \frac{1}{\rho_q^{crit}} \right). \quad (13)$$

Equivalent forms which combine the  $k_{T,pq}$  with the critical temperatures and the  $k_{V,pq}$  with the critical densities are also used:

$$\frac{1}{\rho^*} = \sum_{p=1}^n x_p \frac{1}{\rho_p^{crit}} + \sum_{p=1}^{n-1} \sum_{q=p+1}^n \xi_{pq} x_p x_q, \quad (14)$$

and

$$T^* = \sum_{p=1}^n x_p T_p^{crit} + \sum_{p=1}^{n-1} \sum_{q=p+1}^n \zeta_{pq} x_p^{\beta_{pq}} x_q. \quad (15)$$

If only limited vapor-liquid equilibrium (VLE) data are available the  $a_{pq}^{excess}$  term is taken to be zero, and only the  $k_{T,pq}$  and/or  $k_{V,pq}$  parameters are fitted. The  $k_{T,pq}$  parameter is most closely associated with bubble point pressures, and it is necessary to reproduce azeotropic behavior. The  $k_{V,pq}$  parameter is associated with volume changes on mixing. (Ternary and higher order mixtures are modeled in terms of their constituent binary pairs:  $k_{T,pq} = 1$  and  $k_{V,pq} = 1$  for  $p = q$ .) If extensive data, including single-phase pressure-volume-temperature (PVT) and heat capacity data, are available, the  $a_{pq}^{excess}$  function can be determined. The  $F_{pq}$  parameter is used (either alone or in combination with  $k_{T,pq}$  and  $k_{V,pq}$ ) to generalize the detailed mixture behavior described by the  $a_{pq}^{excess}$  function to other, similar, binary pairs. Lemmon (1996) has determined an  $a_{pq}^{excess}$  function based on data for 28 binary pairs of hydrocarbons, inorganics, and HFC's.

This “mixture Helmholtz-energy model” provides a number of advantages. By applying mixing rules to the Helmholtz energy of the mixture components, it allows the use of high-accuracy equations of state for the components, and the properties of the mixture will reduce exactly to the pure components as the composition approaches a mole fraction of unity. Different components in a mixture may be modeled with different forms; for example, a MBWR equation may be mixed with a Helmholtz equation of state. If the components are modeled with the ECS method, this mixture model allows the use of a different reference fluid for each component. The mixture is modeled in a fundamental way, and thus the departure function is generally a relatively small contribution to the total Helmholtz energy for most refrigerant mixtures. The great flexibility of the adjustable parameters in this model allows an accurate representation of a wide variety of mixtures, provided sufficient experimental data are available.

## B.2 Mixture Critical Parameters

The reducing temperature and density  $T^*$  and  $\rho^*$  in the mixture Helmholtz energy model (Equations 12 – 15) are not the critical parameters for the mixture. The thermodynamic criteria for the critical loci of a binary mixture are

$$\left( \frac{\partial^2 g}{\partial x^2} \right)_{P,T} = 0 \quad (16)$$

and

$$\left( \frac{\partial^3 g}{\partial x^3} \right)_{P,T} = 0 \quad (17)$$

where  $g$  is the molar Gibbs free energy. The solution of these equations is iterative. Equations (16) and (17) have been solved for selected mixtures and the resulting critical loci have been fitted to empirical functions

$$T^{crit} = x_i T_i^{crit} + x_j T_j^{crit} + \sum_{k=1}^6 c_k x_i^k x_j, \quad (18)$$

where the  $c_k$  are fitting parameters; they are stored in the mixture data file and are read upon calling the SETUP subroutine. An analogous function is used for the critical volume. Where these functions are not available, the critical loci are taken to be linear combinations of the pure-component critical parameters (*i.e.* the  $c_k$  are all zero).

For three-component and higher-order mixtures, the thermodynamic criteria for the critical loci become increasingly complicated and time consuming to calculate. The number of possible mixture combinations also increases geometrically with the number of components. These factors make it impractical to store critical surfaces for such mixtures. Instead, REFPROP combines the constituent binary critical lines to approximate the critical parameters by

$$T^{crit} = \frac{\sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j T_{ij}^{crit}(z)}{\sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j}, \quad (19)$$

where the  $T_{ij}^{crit}(z)$  is the binary critical locus for the binary pair (i,j) evaluated at a pseudo-composition  $z$ , based on the mixture composition  $x$



$$z_i = \frac{x_i + (1 - x_j)}{2} \quad (20)$$

and

$$z_j = \frac{x_j + (1 - x_i)}{2} , \quad (21)$$

Again, an analogous expression is used to find the critical volume. This method reduces correctly to the pure-component and binary-pair limits, but is otherwise completely empirical. It yields critical parameters which are approximations, and they should be used with caution.

The critical pressure is calculated from the mixture equation of state given the critical temperature and volume computed by the method outlined above.

### B.3 Surface Tension Model

The surface tension of pure fluids is modeled as a polynomial in the dimensionless temperature  $\tau$

$$\sigma = \sum_{k=0}^n \sigma_k \tau^{d_k} , \quad (22)$$

where

$$\tau = 1 - \frac{T}{T^{crit}} . \quad (23)$$

This form is almost universally used in the literature to represent experimental surface tension data. Often, a summation consisting of a single term, with the exponent on  $\tau$  equal to approximately 1.26, is sufficient to represent surface tension.

For mixtures, the model of Moldover and Rainwater (1988), as implemented by Holcomb (1997), is used. In this method, the pure fluids are assumed to be correlated with a function of the form

$$\sigma_i = \sigma_{0,i} \tau^{1.26} . \quad (24)$$

Although the mixture components may be modeled with a multi-term function, Equation (24) suffices over any limited range of temperature. An “effective”  $\sigma_{0,i}$  for each component is computed for the  $\tau$  of the mixture by using the appropriate pure-fluid model to calculate  $\sigma_i$ . The  $\sigma_{0,i}$  and the critical parameters for the pure components yield the  $C_i$ , a parameter stemming from the Moldover-Rainwater vapor pressure relationship,

$$C_i = \frac{\sigma_{0,i}^{3/2}}{3.74^{3/2} (RT_i^{crit})^{1/2} P_i^{crit} \alpha (1 - \alpha) (2 - \alpha)} , \quad (25)$$

where  $R$  is the gas constant and  $\alpha = 0.1$ . The effective  $C$  for the mixture is given by

$$C_{mix} = \sum_{i=1}^n z_i C_i , \quad (26)$$

where the  $z_i$  is a pseudo-composition based on the fugacity fraction

$$z_i = \frac{f_i}{\sum_{i=1}^n f_i} . \quad (27)$$

The “effective”  $\sigma_0$  for the mixture is then recovered by

$$\sigma_{0,mix} = 3.74(RT^{crit})^{1/3} [C_{mix} P^{crit} \alpha(1-\alpha)(2-\alpha)]^{2/3}, \quad (28)$$

and used in Equation (24) to compute the mixture surface tension. The critical temperature and pressure in Equation (28) are evaluated at a mixture composition having the same fugacity fraction at its critical point as the subject mixture at the input  $(T, x)$ , *i.e.* the  $z_i$  given by Equation (27).

#### B.4 Transport Property Models

The transport properties of viscosity and thermal conductivity are modeled with the residual concept. In this representation, the property  $\Lambda$  (representing either viscosity  $\eta$  or thermal conductivity  $\lambda$ ) is composed of several contributions:

$$\Lambda = \Lambda^{id}(T) + \rho\Lambda^1(T) + \Lambda^r(T, \rho) + \Lambda^c(T, \rho). \quad (29)$$

$\Lambda^{id}$  is a dilute gas term which is a function only of temperature,  $\Lambda^1$  accounts for the behavior at moderate densities, and  $\Lambda^r$  is a residual term accounting for the behavior at higher densities, including liquid densities.  $\Lambda^r$  is primarily a function of density, but it may also be a function of both temperature and density.

The initial density dependence  $\Lambda^1$  follows from the Rainwater-Friend theory (Friend and Rainwater 1984). Although this theory has been developed for both viscosity and thermal conductivity, it is usually applied only to viscosity. The thermal conductivity approaches infinity at the critical point, and this critical enhancement is expressed by  $\Lambda^c$ . This term is significant for thermal conductivity even quite far from the critical point. For viscosity, the enhancement is small except extremely close to the critical point and may be safely ignored in all practical applications.

A variety of models for viscosity and thermal conductivity, based on the residual concept, have been implemented in the database. This section describes, in general terms, the models used. The references listed below or in the pure-fluid information screens in the interface give more details.

#### B.4.1 Pure fluid viscosity models

We have consolidated a variety of fluid-specific correlations for viscosity into a generalized form. The following equations, and also those for thermal conductivity, are written in terms of a reduced temperature  $\tau$  and density  $\delta$  where  $\tau = T/T^{red}$  and  $\delta = \rho/\rho^{red}$ . The viscosity and thermal conductivity also involve reducing parameters  $\eta^{red}$  and  $\lambda^{red}$ . These reducing parameters are used, for example, to convert units, and they may be different for the various terms in each model. The  $a_k$ ,  $b_k$ ,  $d_k$ ,  $t_k$ ,  $e_k$ ,  $l_k$ ,  $m_k$ , and  $n_k$  are adjustable parameters, and the  $C$  represent theoretically based constants.

The dilute-gas contribution is expressed as a combination of the Chapman-Enskog term arising from kinetic theory and an empirical term:

$$\frac{\eta^{id}}{\eta^{red}} = \frac{CM^{1/2}T^{1/2}}{\sigma^2\Omega(T^*)} + \sum a_k \tau^{t_k}, \quad (30)$$

where  $M$  is the molecular weight,  $\sigma$  is the Lennard-Jones size parameter, and we use the empirical function of Bich *et al.* (1987) to represent the reduced effective collision cross section  $\Omega$ :

$$\Omega = \exp \left[ \sum_{i=0}^4 b_i [\ln(T^*)]^i \right], \quad (31)$$

where  $T^* = Tk/\epsilon$  and  $\epsilon/k$  is the Lennard-Jones energy parameter.

The initial density dependence is given by Friend and Rainwater (1984):

$$\frac{\eta^1}{C\sigma^3} = \sum_{i=0}^{12} b_i \left( \frac{T}{\epsilon/k} \right)^{-i/2}. \quad (32)$$

The residual term is expressed as a combination of several empirical terms

$$\frac{\eta^r}{\eta_{red}} = \sum a_k \tau^{t_k} \delta^{d_k} \exp(-\delta^{l_k}) + \frac{\sum a_k \tau^{t_k} \delta^{d_k} \rho_0^{e_k}}{\sum b_k \tau^{t_k} \delta^{d_k} \rho_0^{e_k}} + \exp \left[ \frac{\sum a_k \tau^{t_k} \delta^{d_k} \rho_0^{e_k}}{\sum b_k \tau^{t_k} \delta^{d_k} \rho_0^{e_k}} \right], \quad (33)$$

where the close-packed density  $\rho_0$  is given by

$$\rho_0 = \sum a_k \tau^{t_k}. \quad (34)$$

Equations 30–34 represent, with minor transformations, the viscosity formulations of Laesecke (1997) for R134a, Tanaka (1995) for R123, Fenghour *et al.* (1995) for ammonia, and Krauss *et al.* (1996) for R152a, among others. (Many of the terms are zero for various formulations.) For some of the hydrocarbons, we adopt the fluid-specific formulations of Younglove and Ely (1987). See their paper for a description of this model.

#### B.4.2 Pure fluid thermal conductivity models

The primary model for thermal conductivity represents the dilute-gas and residual terms as rational polynomials

$$\frac{\lambda^{id}}{\lambda^{red}} = \frac{\sum a_k \tau^{t_k}}{\sum b_k \tau^{t_k}} \quad (35)$$

and

$$\frac{\lambda^r}{\lambda^{red}} = \frac{\sum a_k \tau^{t_k} \delta^{d_k}}{\sum b_k \tau^{t_k} \delta^{d_k}} \quad (36)$$

Equations 35 and 36 consolidate into a general form, a variety of fluid-specific correlations, including those of Perkins *et al.* (1998) for R134a, Krauss *et al.* (1996) for R152a, and Laesecke *et al.* (1996) for R123.

The critical enhancement for thermal conductivity is represented using two models. The first is an empirical form used by Laesecke *et al.* (1996):

$$\frac{\lambda^c}{\lambda^{red}} = \frac{\sum a_k (m_k + \tau)^{t_k} (n_k + \delta)^{d_k}}{\sum b_k (m_k + \tau)^{t_k} (n_k + \delta)^{d_k}} + \sum \exp[a_k (m_k + \tau)^{t_k} (n_k + \delta)^{d_k}] \quad (37)$$

The second critical enhancement model is a theoretical form used by Perkins *et al.* (1998) for R134a, Krauss *et al.* (1996) for R152a, and Vesovic *et al.* (1990) for carbon dioxide. We adopt the “simplified” form of this model, as presented by Olchowy and Sengers (1989); it involves the viscosity  $\eta$  and the isochoric and isobaric heat capacities  $C_v$  and  $C_p$

$$\frac{\lambda^c}{\lambda^{red}} = \rho C_p \frac{k R_0 T}{6 \pi \eta(T, \rho) \xi} (\tilde{\Omega} - \tilde{\Omega}_0) \quad (38)$$

where

$$\tilde{\Omega} = \frac{2}{\pi} \left[ \left( \frac{C_p - C_v}{C_p} \right) \tan^{-1}(\tilde{q}_D \xi) + \frac{C_v}{C_p} \tilde{q}_D \xi \right] \quad (39)$$

and

$$\tilde{\Omega}_0 = \frac{2}{\pi} \left\{ 1 - \exp \left[ \frac{-1}{(\tilde{q}_D \xi)^{-1} + 1/3 (\tilde{q}_D \xi \rho^{crit} / \rho)^2} \right] \right\}. \quad (40)$$

The correlation length  $\xi$  is given by

$$\xi = \xi_0 \left[ \frac{\tilde{\chi}(T, \rho) - \tilde{\chi}(T_{ref}, \rho) \frac{T_{ref}}{T}}{\Gamma} \right]^{v/\gamma} \quad (41)$$

where

$$\tilde{\chi}(T, \rho) = \frac{P^{crit} \rho}{(\rho^{crit})^2} \left( \frac{\partial \rho}{\partial P} \right)_T. \quad (42)$$

In Equations 38–42,  $R_0$ ,  $v$ , and  $\gamma$  are theoretically based constants;  $q_D$ ,  $\xi_0$ , and  $\Gamma$  are fluid-specific (fitted) terms;  $T_{ref}$  is an arbitrary reference temperature which is significantly above the critical temperature; and  $k$  is Boltzman's constant.

For some of the hydrocarbons, we adopt the fluid-specific formulations (including dilute-gas, residual, and critical-enhancement terms) of Younglove and Ely (1987). See their paper for a description of this model.

#### B.4.3 Extended corresponding states model for pure fluids

For those pure fluids which do not have wide-ranging, fluid-specific correlations available, REFPROP uses the extended corresponding states (ECS) models of Klein *et al.* (1997) and McLinden and Klein (1998) for viscosity and thermal conductivity, respectively. These models are modifications to the Huber and Ely (1992) and Huber *et al.* (1992) models used in previous versions of REFPROP.

The dilute-gas contributions are given by kinetic theory:

$$\eta^{id}(T) = C \frac{(MT)^{1/2}}{\sigma^2 \Omega^{(2,2)}(kT/\epsilon)} \quad (43)$$

and

$$\lambda^{id}(T) = \frac{f_{int} \eta^{id}(T)}{M} \left[ C_p^{id} - \frac{5}{2} R \right] + \frac{15 R \eta^{id}(T)}{4 M}, \quad (44)$$

where we use the empirical function of Neufeld *et al.* (1972) for the collision integral  $\Omega^{(2,2)}$ , and the  $f_{int}$  is fitted as a linear function of temperature (if sufficient data are available) or set to the constant  $1.32 \times 10^{-3}$ .

As in the ECS model for the thermodynamic properties, the residual parts of the transport properties are based on those of a reference fluid (R134a for the refrigerants in REFPROP):



$$\eta^r(T, \rho) = \eta_0^r(T_0, \rho_{0,\eta}) f^{1/2} h^{-2/3} \left( \frac{M}{M_0} \right)^{1/2} \quad (45)$$

and

$$\lambda^r(T, \rho) = \lambda_0^r(T_0, \rho_{0,\lambda}) f^{1/2} h^{-2/3} \left( \frac{M_0}{M} \right)^{1/2} . \quad (46)$$

The conformal temperature  $T_0$  and density  $\rho_0$  are found by solving Equations 5 and 6; these values are then used to find the reducing ratios  $f$  and  $h$  by Equations 7 and 8. The conformal densities at which the reference fluid formulations are evaluated are modified from those in the thermodynamic ECS model by additional viscosity and thermal conductivity shape factors

$$\rho_{0,\eta} = \Psi(\rho / \rho^{crit}) h \rho \quad (47)$$

and

$$\rho_{0,\lambda} = \chi(\rho / \rho^{crit}) h \rho , \quad (48)$$

where  $\Psi$  and  $\chi$  are empirical polynomials in the reduced density.

The critical enhancement for thermal conductivity is calculated using the method of Olchowky and Sengers (1989).

#### B.4.4 Extended corresponding states model for mixtures

The transport properties of mixtures are modeled with the extended corresponding states (ECS) models of Klein *et al.* (1997) and McLinden and Klein (1998) for viscosity and thermal conductivity, respectively. These models are modifications to the Huber and Ely (1992) and Huber *et al.* (1992) models used in previous versions of REFPROP.

Mixture transport properties are composed of the same terms present for the pure fluids. The dilute-gas contribution is calculated by matrix analogs of Equations 43 and 44; see, for example, Hirschfelder *et al.* (1967). All quantities in the dilute-gas terms are evaluated at the temperature of the mixture, rather than some conformal temperature.

The residual contribution is found by combining the properties of the reference fluid, evaluated at the conformal conditions given by the solution of:

$$\alpha_0^r(T_0, \rho_0) = \alpha_{mix}^r(T, \rho, x) \quad (49)$$

and

$$Z_0(T_0, \rho_0) = Z_{mix}(T, \rho, x) \quad (50)$$

with the viscosity or thermal conductivity of each of the components, evaluated at the conformal conditions given by

$$\alpha_j^r(T_j, \rho_j) = \alpha_{mix}^r(T, \rho, x) \quad (51)$$

and

$$Z_j(T_j, \rho_j) = Z_{mix}(T, \rho, x) \quad (52)$$

where the subscripts 0 and  $j$  refer to the reference fluid and component  $j$  in the mixture, respectively. The reducing parameters are then defined by

$$f_x = \frac{T}{T_0} , \quad (53)$$

$$h_x = \frac{\rho_0}{\rho} , \quad (54)$$

$$f_j = \frac{T_j f_x}{T} , \quad (55)$$

and

$$h_j = \frac{\rho h_x}{\rho_j} . \quad (56)$$

The ratio of molar masses  $(M_0/M)^{1/2}$  in equations 45 and 46 is replaced by

$$g_x^{1/2} = \frac{M_0^{1/2} f_x^{1/2} h_x^{4/3}}{\sum_{i=1}^n \sum_{j=1}^n x_i x_j (f_i f_j)^{1/2} \left( \frac{2}{1/g_i + 1/g_j} \right)^{1/2} \left[ \frac{1}{8} (h_i^{1/3} + h_j^{1/3})^3 \right]^{4/3}} , \quad (57)$$

where

$$g_i = M_0 \left[ \frac{\Lambda_0^r(T_0, \rho_0)}{\Lambda_j^r(T_j, \rho_j)} \right]^2 f_j h_j^{-4/3} . \quad (58)$$

Again, the  $\Lambda$  represents either viscosity or thermal conductivity. Including the pure component values in this way ensures that the properties of a mixture reduce to the pure fluid values as the composition approaches 1.

## B.5 References

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